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HIGH-TEMPERATURE

OXIDATION PROTECTIVE COATINGS

FOR VANADIUM-BASE ALLOYS

Contract N600(19)59182

ARF-B6001-2

(Bimonthly Report No. 2)

Department of the Navy

Bureau of Naval Weapons

Washington 25, D. C.

Attention: Code RRMA-222

ARMOUR RESEARCH FOUNDATION
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ILLINOIS INSTITUTE OF TECHNOLOGY
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HIGH-TEMPERATURE OXIDATION PROTECTIVE COATINGS FOR VANADIUM-BASE ALLOYS

Contract N600(19)59182
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(Bimonthly Report No. 2)
November 13, 1962 - January 12, 1963

Department of the Navy
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February 9, 1963

HIGH-TEMPERATURE OXIDATION PROTECTIVE COATINGS FOR VANADIUM-BASE ALLOYS

ABSTRACT

Processing variables relating to the pack-siliconizing of V-5w/o Ti-20w/o Cb and V-1w/o Ti-60w/o Cb are being studied. Samples coated at 2010°, 2190°, and 2370°F show that coating growth rate is time dependent up to 16 hours. Silicide coatings have been applied to eleven vanadium alloys currently under development, and no failures have been observed after 15 to 35 hours in 2200°F air. Tensile and other specimens of V-1w/o Ti-60w/o Cb have been pack-siliconized for evaluation by aerospace and other organizations.

Compounds of V-Cb-Ni were flame-sprayed on V-1w/o Ti-60w/o Cb, but excessive porosity caused rapid failure in 2000° and 2200°F air. Diffusion couples of nickel and the V-Cb-Ti alloy were reacted at 2000° and 2200°F for 24 and 8 hours, respectively, with very slight hardening of the vanadium alloy.

HIGH-TEMPERATURE OXIDATION PROTECTIVE COATINGS FOR VANADIUM-BASE ALLOYS

I. INTRODUCTION

This is the second bimonthly progress report under Contract No. N600(19)59182, summarizing the work performed on ARF Project B6001 during the period November 13, 1962 to January 12, 1963

Efforts are being devoted to optimizing the highly-promising silicide coatings for vanadium-columbium alloys. The reliability of these coatings on several of the higher-strength alloys will be evaluated in detail after a study of coating processing variables has been completed. Vanadium alloy specimens will also be coated for evaluation by aerospace and other organizations participating in the data-exchange program under Contract NOw 62-0101-c, "Pilot Evaluation of Vanadium Alloys."

To date, the most promising vanadium-columbium alloys are V-1Ti-60Cb and V-4Ti-20Cb-1Zr-0.075C,* and 100-pound ingots of these compositions have been fabricated to sheet under the pilot evaluation program. Other compositions currently under study include additions of tantalum and other refractory metals to a V-60Cb base containing 1w/o zirconium or hafnium. Silicide coatings are being applied to these experimental alloys so that coatability will be established before selection of a composition for the third large (100- or 150-pound)ingot for pilot evaluation.

Experimental work under this program also includes a brief investigation of nickel-base coatings on V-1Ti-60Cb. Since earlier work had shown that flame-sprayed nickel was protective for more than 100 hours in air at 2000°F, recent studies have been devoted to establishing the upper temperature limit of usefulness of this coating. Similar work has also been performed on coatings containing cobalt, and on coatings based on vanadium-columbium-nickel compounds.

* Compositions are reported in weight per cent.

II. EXPERIMENTAL RESULTS AND DISCUSSION

A. Silicide-Base Coatings

1. Investigation of Processing Variables

Recent effort has been expended investigating processing variables in an attempt to optimize our basic pack-cementation siliconizing process. This work is in preparation for the coating and evaluation of specimens according to the procedures outlined by the Materials Advisory Board[1] and for the coating of test specimens which are being supplied by other organizations.

In this study, pack and retort design, activator species and concentration, silicon powder size and quantity were kept constant while studying the influence of temperature, time, and surface preparation techniques. Specimens of the V-1Ti-60Cb and the V-5Ti-20Cb alloy were siliconized at 2010°, 2190° and 2370° F for 4, 8, and 16 hours. Surface preparation consisted of tumbling the specimens in an alumina grit slurry for 100 hours followed by etching in $25HNO_3$-$5HF$-$70H_2O$, with a subsequent water and acetone rinse. Weight gain and thickness measurements were made for the specimens prepared under these conditions. The coating growth rate is time dependent, for times up to 16 hours, at all of the temperatures studied. A marked temperature dependence was also observed. Figures 1 and 2 show the silicide layers formed on the V-5Ti-20Cb alloy during coating at 2190° F for 8 hours, 2.5 mil thickness, and 16 hours, 4.0 mil thickness, respectively. In Figure 3, the coating layer formed during siliconizing at 2370° F for 4 hours, a thickness of 3.0 mils, may be seen. Each coating consists of at least two layers, the innermost one ranging in thickness from 0.1 to 0.4 mils. The outermost layer is generally cracked and contains numerous voids and inclusions. Cracking is rarely observed in the innermost layer.

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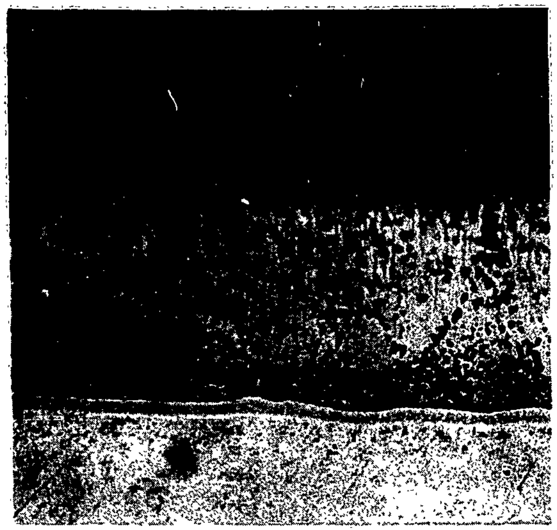
(2) "Evaluation Procedures for Screening Coated Refractory Metal Sheet," Materials Advisory Board Sub-Panel Coatings, September 1962.



Neg. No. 24247 X500

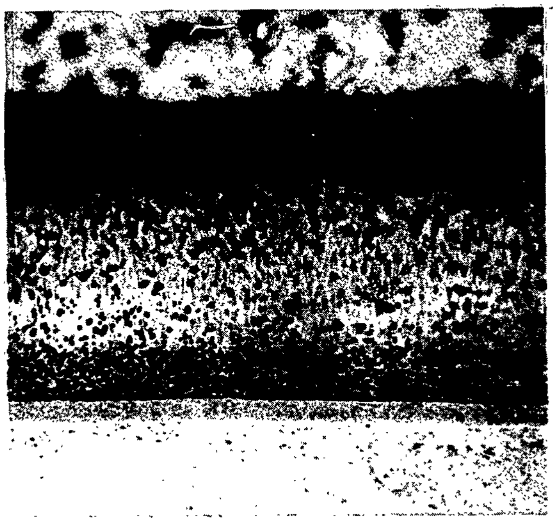
Fig. 1

V-5Ti-20Cb, pack siliconized at 2190°F for eight hours.

Neg. No. 24248 X500

Fig. 2

V-5Ti-20Cb, pack siliconized at 2190°F for sixteen hours.



Neg. No. 24244 X500

Fig. 3

V-5Ti-20Cb, pack siliconized at 2370°F for four hours.

Neg. No. 24246 X500

Fig. 4

V-1Ti-60Cb, pack siliconized at 2190°F for eight hours.

The structure of siliconized V-1Ti-60Cb after treatment at 2190° F for 8 hours may be seen in Figure 4. At least one additional diffusion layer exists in this alloy which is not present in the siliconized V-5Ti-20Cb alloy. In every case, cracking appears to be confined to the two outermost layers.

Microhardness measurements made on the siliconized alloys show that the hardness of all diffusion layers exceeds 1150VPN.

Oxidation-test results indicate that processing at 2200° F for 16 hours appears to be optimum for both alloys, although treatment at a higher temperature may be comparable. The test results further indicate that specimens produced under these conditions show a greater incidence of failure and over-all shorter life than those which were processed similarly in previous work. The difference may be due to the surface preparation technique employed. This is currently under investigation. An additional parametric study under way is determination of the influence of double processing on coating performance.

2. Oxidation Behavior of Additional Siliconized Alloys

Alloys which are currently being developed under Contract NOw 62-0101-c, are being siliconized to determine the protective capability it affords. Small test coupons have been coated by siliconizing at 2190° F for 16 hours. The alloys which have been coated include:

V-1Hf-60Cb	V-20Cb-5Ti-5W
V-1Ti-60Cb-0.075C	V-20Cb-4Ti-1Zr
V-1Hf-60Cb-0.40O	V-20Cb-4Ti-1Zr-0.07C
V-1Hf-60Cb-10Ta	
V-1Ti-60Cb-0.5Ru-2.5Mo	V-10Cb-10W
V-1Ti-70Cb	V-40Cb-30Ta-1Hf

The specimens are being tested at 2200° F in static air with periodic examinations. Alloys have been exposed for times varying between 15 and 35 hours. No failures have been observed, as yet. Specimens of additional alloys are currently being siliconized, and will also be exposed to 2200° F air. As alloy development efforts continue, the most promising

compositions will be coated and subjected to more complete evaluations, in order to insure that the alloy selected for the third large (100-pound) ingot can be adequately protected by the pack-cementation silicide coating.

Other efforts under this program include the siliconizing of bend, tensile, stress-rupture, and other specimens prepared from sheet fabricated from the 100-pound ingot of V-1Ti-60Cb. This work is being coordinated under Contract NOw 62-0101-c, "Pilot Evaluation of Vanadium Alloys". Specimens up to 8-inches long are currently being coated, and will be forwarded to the aerospace and other organizations participating in the data-exchange portion of the pilot evaluation program. Results of these evaluations of coated specimens will be presented in reports issued under NOw 62-0101-c, and pertinent information will also be discussed in reports under this oxidation-protective coatings program.

B. Other Coatings Systems

During the previous year's work under Contract NOw 61-0806-c, the only coating (other than the silicide-base materials) that exhibited noteworthy defect-tolerating ability and protective capabilities above 2000°F was nickel, when flame-sprayed on V-1Ti-60Cb. To further assess the factors involved in this coating system, the oxidation behavior of compounds based on V-Cb-Ni was investigated, and diffusion couples between the Ni and V-1Ti-60Cb were studied. The more oxidation-resistant V-Cb-Ni compounds were flame-sprayed on V-1Ti-60Cb and exposed to air at 2000°F. In addition, cobalt was studied as a flame-sprayed coating, and V-Cb-Co compounds were also prepared in order to evaluate their oxidation behavior.

1. V-Cb-Ni Compounds

Nonconsumable-electrode arc-melted ingots of V-Cb-Ni were prepared for a study of oxidation behavior and for use in subsequent flame-spraying experiments on V-1Ti-60Cb. These compositions were based on VNi_2 and VNi_3, and columbium was added in varying amounts to replace vanadium. Most of these compositions had weight gains of well below 2w/o in 24 hours at 2000°F. Two of the most oxidation-resistant compounds were selected for flame-spraying experiments. Previously it had been found that when nickel was flame-sprayed on V-1Ti-60Cb and subsequently heated at

2000°F, the oxidation-protective V-Cb-Ni compound layers which formed tended to pull away from the base because of thermal expansion. Consequently, it was decided to prepare the V-Cb-Ni compounds in powder form, then flame-spray them on the alloy base. Efforts to do this were hampered because the compounds were slightly ductile (but not hot-workable) and could not readily be crushed into a fine powder. Even after hydrogenation, the compounds (Ni-10.5V-28.75Cb and Ni-10.3V-18.75Cb) were not brittle enough to be crushed to the desired -325 mesh particle size. A sufficient quantity of -120 mesh was prepared, however, and flame-sprayed on the V-1Ti-60Cb base. The relatively high porosity of these coatings led to failure within 30 minutes in air at 2000° and 2200°F. It is believed that finer powders can be produced in an apparatus employing a sintered tungsten-carbide bur rotating under an inert atmosphere, and this unit will be used in subsequent experiments.

2. V-Cb-Co Compounds

Since V-Co and Cb-Co compounds have somewhat higher melting points than similar compounds in the V-Ni and Cb-Ni system, ternary V-Cb-Co compounds were prepared by arc-melting. These compositions were based on VCo_2 and VCo_3, and columbium was added to replace part of the vanadium. After a 24-hour exposure to 2000°F air, weight gains were in the 7 to 18 per cent range compared to about 1 to 2 per cent for the nickel-containing compounds. A few specimens also exhibited a liquid oxide. The oxidation resistance of the (V, Cb) Co_3 compositions was higher than that of the (V, Cb) Co_2 alloys. However, none were sufficiently oxidation resistant to warrant testing at temperatures above 2000°F.

3. Diffusion-Couple Studies

To further investigate reactions between nickel and cobalt and the V-1Ti-60Cb alloy, a series of diffusion couples was prepared, reacted at 2000° and 2200°F, and evaluated for hardness and structure. Table I summarizes the results of microhardness surveys; measurements were taken in the intermetallic compound layer between the pairs, and also in the vanadium-columbium alloys at varying distances from the interface. The 2000°F treatments for 24 hours produced far less hardening of the vanadium

TABLE I

HARDNESS DATA FOR DIFFUSION COUPLES

Diffusion Pair	Heat Treatment[a] Temp, °F	Time, hr	Microhardness Location	VPN(50g)[b]
Ni + V-1Ti-60Cb	2000	24	In compound	532
			In alloy, 100μ from interface	447
			In alloy, 500μ from interface	412
Ni + V-1Ti-60Cb	2200	8	In compound	909
			In alloy, 100μ from interface	509
			In alloy, 500μ from interface	391
Co + V-1Ti-60Cb	2000	24	In compound	1072
			In alloy, 100μ from interface	557
			In alloy, 500μ from interface	509
Co + V-1Ti-60Cb	2200	8	In compound	1049
			In alloy, 100μ from interface	810
			In alloy, 500μ from interface	666

a. In argon atmosphere

b. Base hardness of V-1Ti-60Cb alloy about VPN (50g) 400.

base than did the 8-hour treatments at 2200° F. Reaction with nickel produced relatively little hardening of the alloy, while cobalt at both temperatures hardened the V-1Ti-60Cb excessively. These data indicate that cobalt is not suitable as a coating and that nickel on the alloy base must not be used much above 2000° F (very short exposures may be tolerated at 2200° F).

III. SUMMARY

Major efforts under this program are concerned with pack-cementation siliconized coatings for vanadium-base alloys. A study of coating processing variables was continued, using specimens of V-5Ti-20Cb and V-1Ti-60Cb. Samples coated at 2010°, 2190° and 2370° F show that coating growth rate is time dependent for times up to 16 hours at these temperatures. Oxidation test results indicate that processing at 2200° F for 16 hours is optimum for both alloys. The practice of tumbling specimens in an alumina slurry prior to etching and coating may possibly affect coating performance; this factor is under investigation.

Vanadium alloys currently being developed under Contract NOw 62-0101-c have been siliconized at 2190° F for 16 hours. Eleven compositions have been coated and exposed to 2200° F air with no evidence of failure in times of 15 to 35 hours. Other efforts related to the alloy development and pilot evaluation include the siliconizing of V-1Ti-60Cb bend, tensile, and stress-rupture specimens to be evaluated by other organizations.

Efforts were also devoted to a study of coating systems based on nickel and cobalt, since earlier work had indicated promise for nickel when flame-sprayed on V-1Ti-60Cb. Arc-melted V-Cb-Ni compositions exhibited weight gains ranging from less than 1 per cent to about 2 per cent in 24 hours at 2000° F. Two of these alloys were comminuted to pass 120 mesh, then were flame-sprayed on a V-1Ti-60Cb base. The porous nature of these coatings caused rapid failure when exposed to 2000° F air; finer powders (and more dense coatings) could not be produced by crushing because the compounds were slightly ductile. A similar series of V-Cb-Co compositions exhibited very high weight gains (7 to 18 per cent) in 24 hours in 2000° F air. Diffusion couples between nickel and V-1Ti-60Cb, reacted for 24 hours at 2000° F and 8 hours at 2200° F, exhibited very slight hardening

of the alloy base. Reactions between cobalt and V-1Ti-60Cb, after the same heat treatments, caused excessive hardening of the V-1Ti-60Cb.

IV. FUTURE WORK

A number of tab specimens, 1 1/2 x 3/4 x 0.020 in. of the V-5Ti-20Cb and V-1Ti-60Cb alloy have been prepared for siliconizing. When the results of our present processing variables study are complete, particularly with respect to surface preparation techniques, these will be coated and oxidized in static air and an oxygen-acetylene flame at temperatures to 3200° F. Mechanical properties of the coated alloys will also be determined under a variety of conditions. We will continue to supply coated test samples to interested and qualified organizations participating in the data-exchange program.

Determination of the oxidation behavior after siliconizing, of alloys being developed under Contract NOw 62-0101-c, will continue. These determinations will be made for static air exposures, however, the more interesting alloys will be tested at higher temperatures under dynamic conditions.

Further work on the evaluation of Ag-Si slurry coatings is planned. Specimens will be prepared and subjected to some of the tests planned for the pack-siliconized specimens.

Efforts on nickel-containing coatings will be limited to the preparation of an arc-melted V-Cb-Ni ingot, which will be comminuted to pass -325 mesh using new powder preparation techniques. If a sufficient quantity of the fine powder can be obtained, it will be flame sprayed on V-1Ti-60Cb.

V. LOGBOOKS AND PERSONNEL

Data for this report are recorded in ARF Logbooks C-12904 and C-13008.

The following personnel have been the principal contributors to the planning and execution of this work:

A. L. Hess	-	Project Technician
F. C. Holtz	-	Project Leader
L. I. Kane	-	Technical Assistant
J. J. Rausch	-	Silicide-Base Coatings

Respectfully submitted,

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